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NRA-03-OSS-01-APRA Astronomy and Physics Research and Analysis

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2 Summary of Personnel and Work Efforts

The principal investigator has worked in the field of molecular spectroscopy for eight years. He is employed at the Jet Propulsion Laboratory as a scientist in the molecular spectroscopy group. A two to three year postdoctoral appointment will fill the remaining personnel requirements. During the three year funding period the time contributed is seventy-five percent of one full time employee per year (0.75 FTE).

Table 1: Summary of Staffing Request by Government Fiscal Year:

	FY '04	FY '05	FY '06
PI BJ Drouin	25%	25%	25%
Postdoctoral	50%	50%	50%

Dr. Brian Drouin is a co-investigator for the Earth Observing System (EOS) Spectroscopy program and a Microwave Limb Sounder (MLS) Science Investigator, programs that require 60% of his current time. Starting in FY '04 he intends to fill the PI role in the spectroscopy in support of upper atmospheric research program (UARP).

The postdoctoral position will be divided among this proposed effort and the UARP task.

3 Scientific/Technical/Management

3.1 Objectives and Expected Significance

This laboratory task will support the continuing effort to understand the diversity of other worlds and search for those that might harbor life. In particular this effort is necessary for two research focus area of the **Astronomical Search for Origins**

2.(c) - *Trace the chemical pathways by which simple molecules and dust evolve into the organic molecules important for life.*

2.(d) - *Develop the tools and techniques to search for life on planets beyond our Solar System.*

The **Astronomy and Physics Research and Analysis program (APRA)** pursues these NASA goals through support of tasks to develop supporting technology, **perform laboratory research**, and/or conduct ground based observations that are directly applicable to space astrophysics missions. The proposed laboratory research will improve the spectroscopic database for three molecules. Parameters, *i.e.* rest frequencies, used for identification of molecular species in the universe will be obtained with laboratory measurements combined with quantum-mechanical models that allow fitting and interpolation. Predicted and experimental rest frequencies will be incorporated into the JPL Spectral Line Catalog and published in peer-reviewed literature. These results are needed for ground based observational astronomy in the microwave and millimeter regions. These data will become acutely important in the submillimeter and Far-Infrared regions with the implementation of wide-band spectrometers on board the NASA observatories **Herschel (HSO)** and Stratospheric Observatory for Infrared Astronomy (**SOFIA**).

Observations of chemical pathways that trace the origins of organic molecules important for life in the universe are made possible *only* through interpretations of molecular spectra in astronomical sources. Over one hundred and twenty distinct molecules have been identified in interstellar sources. Protostellar regions are the birthplaces of new solar systems, and hence the best place to study chemical evolution pathways that may lead to origins of life. By virtue of the molecular spectra, observers can identify the composition, structure, age, dynamics, and, of course, chemistry, of these systems. Nevertheless, roadblocks in our knowledge of complex molecular spectra remain. Several relatively simple molecules, known to exist in protostellar regions, have rich, complex spectra that are parameterized only for the ground vibrational state. Molecules with low energy vibrational-torsional states will have significant population of these levels in hot, dense molecular cores of protostellar regions. This poses both possibilities and problems for the research focus areas outlined above.

These possibilities lie in the development of tools and techniques to study chemistry, energetics and composition in the universal laboratory. Chemical studies will follow from the study of organic compounds that contain key functional groups; *i.e.* carboxylic acids, ethers and ketones, that are essential building blocks of biological molecules. Furthermore, column abundances used to constrain chemical models will be more accurate with the inclusion of vibrational-torsional states. Energetics inherent to the physics of vibrational-torsional states and their interactions will allow studies of differences in rotational temperature (T_R) and vibration-torsional temperature (T_v). Such information can elucidate the local thermodynamic environment and help determine excitation mechanisms. Chemical composition and chemical discovery within interstellar regions will be improved through better identification of previously unknown features made available through the proposed research. Chemical models that take advantage of these

observational tools will more clearly mark the chemical pathways that lead to life.

A large problem in these intensely studied protostellar regions is associated with the existence of molecules with a high density of states at low energy (< 300 K or 208 cm^{-1}). The partition of these molecules into the low energy states produces duplicate spectra, each just as complex as the ground state, for each populated state.

With the lack of complete spectroscopic rest frequency listings of such states, the large number of unidentifiable features has resulted in line confusion and contributed significantly to the molecular continuum. Line confusion, or molecular continua, or both, refer to the level of integration at which a search for known molecular signatures becomes ambiguous, or impossible due to the discovery of unidentifiable, interfering signatures that congest the spectral region. With better knowledge of these crowded, although *not necessarily confused* spectral regions, currently undetected (with intensities near the molecular continuum) species will be discerned. Astronomers prefer to avoid congested spectral regions prior to conducting observations. Nevertheless, successful choice of a free region is based on known, tabulated, rest frequency listings of identified molecules in the source of interest. **It is the hypothesis of this proposal that a large number of these ubiquitous unknown signatures could be conclusively identified provided the spectroscopic information is sufficiently complete and accurate.** Depending on the number of available states and ambient temperature, anywhere from 2 - 10x the number of ground state rest frequencies may be necessary to characterize all of the rest frequencies recorded for a particular molecular species. Acetone, has over 11000 rest frequencies listed for the ground state below 630 GHz[Groner, *et al.* 2002], however, the number of rest frequencies necessary to characterize all of the acetone features (below 630 GHz) in a source of 170 K[Snyder, *et al.* 2002] is approximately 45000.

Three molecules; acetic acid (CH_3COOH), dimethyl ether($(\text{CH}_3)_2\text{O}$), and acetone ($(\text{CH}_3)_2\text{CO}$), have been chosen for investigation because each is considered to be a building block of organic chemistry, and to have potential for elucidation of chemical pathways[Charnley, 1997, Charnley, 1999]. Each of the species has been discovered (with millimeter wave ground state rest frequencies) in the interstellar molecular havens known as hot cores, Large Molecular Heimats (LMHs) or compact ridges; areas where temperatures may reach 300 K and local thermodynamic equilibrium (LTE) is often a reasonable assumption[Blake, *et al.* 1987].

Acetic acid (CH_3COOH) has been identified in the hot cores Sgr B2(N-LMH)[Mehring, *et al.* 2002] and W51e2[Remijan, *et al.* 2002]. The molecule is of special interest to chemical evolution and biological origins because of its structural similarity to glycine as well as its chemical isomerism with methyl formate[Mehring and Snyder 1996, Miao, *et al.* 1995, Liu, *et al.* 2000] and glycoaldehyde[Hollis, *et al.* 2000], of which the relative abundances remain ill-understood. Glycine has not yet been identified in any interstellar sources, although acetic acid and its isomers have, and are believed to be involved in chemical pathways for creation of amino acids[Charnley, 1999]. The most recent spectroscopic study[Ilyushin, *et al.* 2001] has combined previous work and listed the necessary spectral parameters for identification of rest frequencies in the ground and first vibrational-torsional (v_t) state up to *ca.* 400 GHz, where; $v_t = 1$, $E_1(A) = 79.1\text{ cm}^{-1}$, $E_1(E) = 72.8\text{ cm}^{-1}$. Nevertheless, as noted in Ilyushin *et al.*, the $v_t = 1$ state rest frequencies remain suspect when interpolated, and the next low-energy state; $v_t = 2$, $E_2(A, E) \sim 120\text{ cm}^{-1}$, remains un-analyzed. Since there may be a series of vibrational-torsional rest frequencies at significantly different lower state energies within small frequency windows, astronomers will be likely to observe these in normal searches for the ground state features. Identification and analysis of these vibrational-torsional state rest frequencies will undoubtedly lead to a better

understanding of the physical properties of the region and its chemical environment. Because of the limited range of laboratory measurements of 360 GHz, new spectra, at higher frequencies, will need to be recorded, analyzed and interpolated for parameter listings. This may allow identification of acetic acid spectra with the NASA observatories that operate above 480 GHz.

Dimethyl ether ($(\text{CH}_3)_2\text{O}$) has been identified in a variety of interstellar sources including galactic center [Mehringer, *et al.* 2002, Snyder, *et al.* 1994]. This species is found in cold, diffuse regions, as well as in warmer regions such as the compact ridge of Orion [Ikeda, *et al.* 2001]. This presence in a variety of interstellar sources has lead to the hypothesis that it is an initial synthetic product of methanol and methyl cation after desorption of methanol from grain surfaces. Therefore, the abundance of dimethyl ether can be useful for determining the age of the interstellar region. In warm, dense regions dimethyl ether will (assuming LTE) have population in the first vibrational torsional state. The recent ground state analysis of Groner *et al.* [Groner, *et al.* 1998] has created a solid framework for further analysis of both the first vibrational-torsional state and higher frequency spectra. The framework is based on the development of a symmetry restricted model [Groner, 1997] that incorporates the internal kinetic and potential energies of the two methyl rotors into the overall rotation of the molecule. Not only will this readily allow fitting and interpolation of new spectra to be measured at higher frequencies, but will also enable extension of the model to higher quantum numbers and other vibrational-torsional states. The listing of vibrational-torsional state rest frequencies will curb problems such as the difficulty of comparison of observed abundances with kinetic gas temperatures [Ikeda, *et al.* 2001]. In addition to the proposed comprehensive analysis of the first vibrational-torsional state spectra up into the submillimeter wavelengths, the current range of laboratory measurements (550 GHz), will be extended (to at least 900 GHz), analyzed and interpolated. Otherwise, the present parameter listings will only cover dimethyl ether spectra within the lowest frequency ranges of NASA observatories that operate above 480 GHz.

Acetone ($(\text{CH}_3)_2\text{CO}$) has only recently been confirmed as an interstellar species [Snyder, *et al.* 2002] based on the thorough ground state analysis of [Groner, *et al.* 2002]. The abundances measured in Sgr B2 (N - LMH) are large and cannot be explained by gas-phase ion-molecule syntheses. This was not unexpected as other oxygen containing organic compounds in compact interstellar regions have also shown unexplained large abundances [Herbst, *et al.* 1990]. The authors [Snyder, *et al.* 2002] indicate the need for more study of acetone to allow a better understanding of the underlying chemistry. The model used for spectral analysis and parameter determination of acetone is based upon that of dimethyl ether. However, acetone poses more fundamental problems that translate into drastic issues for observational astronomy. Unlike dimethyl ether, the barrier to internal rotation of the methyl groups is intermediate, as opposed to the more readily modelled low- and high- barrier situations. Consequently, models that effectively parameterize the rotational-torsional spectra converge slowly and often interpolate poorly. Acetone also has more low-energy vibrational-torsional states (*ca.* 80 cm^{-1} , 124 cm^{-1} , 150 cm^{-1} , 177 cm^{-1} and 230 cm^{-1}) that are significantly populated at temperatures found in hot cores or compact ridges. Ignorance of these states will lead to errors in column abundance, energy distributions and chemical modelling. The situation is exemplified by reproduction of a figure (see Figure 1) from Snyder *et al.* [Snyder, *et al.* 2002], wherein several unidentified signatures are noted. Comparison with a laboratory spectrum (see Figure 2) of acetone, taken with the JPL millimeter and submillimeter spectrometer at 295 K, shows remarkable coincidences of unidentified features. Since the laboratory spectrum was taken with a pure sample, it is likely that these unidentified features are attributable to excited vibrational-torsional states that are

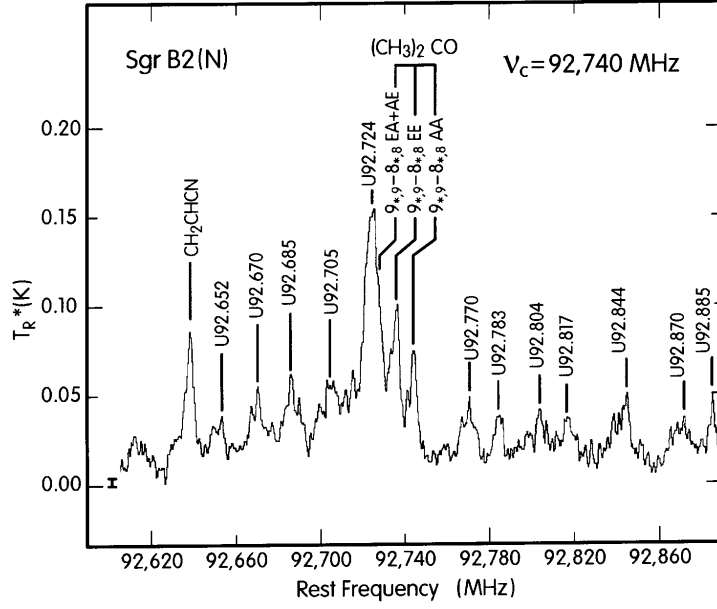


Figure 1: NRAO 12 m spectra of Sgr B2 (estimated to be 170 K) containing emission spectra of acetone and other species. The ordinate is T_R , and the abscissa is rest frequency calculated with respect to VLSR = 64.0 km s⁻¹. The rms noise level is 0.005 K, as indicated by the small vertical bar on the left. Reproduced from [Snyder, *et al.* 2002].

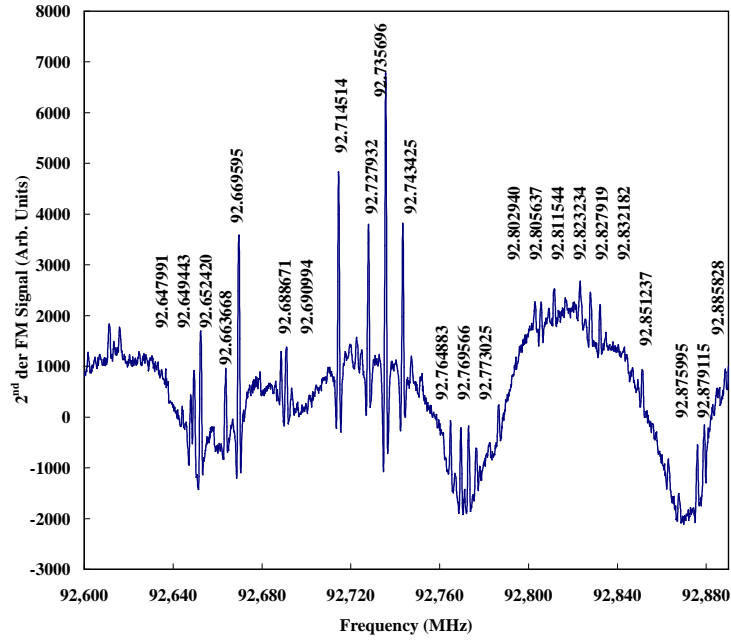


Figure 2: JPL spectrum of acetone at 295 K. The ordinate is 2nd derivative FM detected signal in arbitrary units, the abscissa is the phase locked source frequency.

populated at 295 K. A hypothetical situation for a spectrum taken with Band 1 of the Herschel telescope’s HIFI instrument exasperates the problem further. Given the column abundance from Sgr B2 (N - LMH), $\langle N_T \rangle = 2.9(3) \times 10^{16} \text{ cm}^2$ [Snyder, *et al.* 2002], and given a sufficiently low (dust) continuum level, HIFI could observe the $J = 29, K = 0, 1$ multiplet near 605 GHz with a signal to noise ratio (SNR) of 10 with an integration time of one second. Based on torsional level energies [Groner, 2000], similar strength transitions ($\text{SNR} > 1$), at currently unknown positions, that arise from only the lowest energy vibrational torsional states will be observed at a rate 4.5 times the rate of analogous ground state features for this 170 K source. The current range of laboratory measurements extends to 620 GHz; new spectra, at higher frequencies, will need to be recorded, analyzed and interpolated for rest frequency listings. This will allow more better coverage of ground state acetone spectra with the NASA observatories that operate only above 480 GHz.

The location of this molecular spectroscopy laboratory at the JPL NASA center insures that cutting edge research will be accomplished as only NASA can. The concurrent development and testing of the Herschel space telescope allows this molecular spectroscopy laboratory access to the best (*i.e.* stable, powerful and simple) sources for heterodyne quality spectroscopic measurements throughout the submillimeter wavelengths and into the Far-Infrared. Furthermore, the legacy of the JPL Spectral Line Catalog and its powerful analysis software, is maintained through this laboratory. In general, complex molecular spectra are analyzed with a variety of different techniques. Only the JPL/NASA maintained SPFIT/SPCAT software is capable of processing radically different types of molecular spectra within one basic framework. For development of a trusted and robust database such as JPLs Spectral Line Catalog, the importance of this single basic framework cannot be understated.

3.2 Technical Approach and Methodology

The proposed work is to be done with the spectrometer and software at the Millimeter, Submillimeter and Far-Infrared Spectroscopy Laboratory at JPL and will be made freely available to the NASA community and public domain through peer-reviewed publications and full rest frequency listings on the JPL Spectral Line Catalog www and ftp server. The work will be directed toward progress in the understanding of molecular rest frequencies for complex spectra of critical need to NASA astrophysics missions. The analyses of the spectra will culminate in comprehensive listings of the necessary molecular parameters that will be fundamentally important to **astrophysical search for origins**, molecular physics and quantum chemistry through elucidation of the molecular rest frequencies, inertial moments, kinematic intramolecular interactions and potential barrier heights. Furthermore these parameters will also be useful in describing the physical chemical properties of the molecules.

The JPL millimeter and submillimeter spectrometer will be used for measurements of spectra mentioned in the scientific plan. The spectrometer employs active and passive multiplier chains to generate tunable monochromatic source frequencies. The millimeter or submillimeter beam is launched through a free space cell that can be temperature controlled in the 180 - 370 K range. Gas for study is flowed through the free space cell while the frequency source is swept with computer control. A vacuum pump is used to reduce pressure of pure gas samples to avoid collisional broadening, leading to rest frequency measurements that are limited only by Doppler broadening. Modulation of the source frequency allows phase-sensitive detection of the molecular absorption features with a diode detector (70 – 170 GHz, 2 – 4 mm) or a liquid helium cooled InSb bolometer (> 170 GHz, < 2 mm) followed by a lock-in-amplifier. The system is capable of

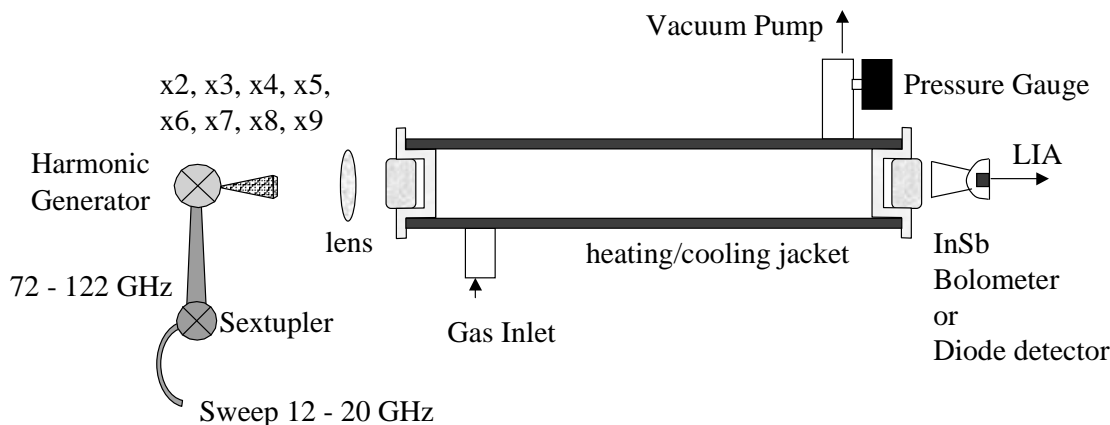


Figure 3: A schematic showing key parts of the JPL millimeter and submillimeter spectrometer. Different, tunable harmonic generators are available for selective production of the various frequency multiples. The dual window design insures temperature homogeneity within the free-space cell. LIA refers to the Lock-In-Amplifier used for phase sensitive detection of the frequency modulated source signal.

recording vast ranges of spectral data (up to 50 GHz in a single scan) of different molecules at multiple temperatures.

Frequency multipliers and amplifiers, both commercial and JPL-built, enable comprehensive frequency coverage from 70 - 700 GHz (0.4 - 4 mm). Selected frequency ranges are also available up to 1 THz. Frequency multipliers in the 500+ GHz region [Oswald, *et al.* 1998], as well as amplifiers in the 100 GHz range [Wang, *et al.* 2001] have been made available through collaborative efforts with JPL laboratories (Submillimeter Wave Astronomy Team and Submillimeter Superconducting Sensors Group) that are developing and testing hardware for the Herschel mission. At the core of the spectrometer an Agilent sextupler (83558A) replaces the traditional phase-locked millimeter wave Klystron sources. The 83558A combined with an RF sweep synthesizer can produce 0.1 - 1 mW in the WR-10 band and beyond (70 - 115 GHz). Coupling the sextupler with JPL amplifier technology [Wang, *et al.* 2001] allows 1 - 10 mW of power for production of harmonic frequencies with whisker and planar Schottky diode multipliers.

Dimethyl ether has the best understood of the spectra proposed to be studied in this work. Therefore, this species will be the first studied, for the dual purpose of refining the model required for acetone, and for training of the postdoctoral fellow. During measurement and analysis of dimethyl ether by the postdoctoral fellow, the principal investigator will begin SPFIT/SPCAT analyses of the literature data of the remaining species. These analyses should reproduce the cumulative works of Refs [Ilyushin, *et al.* 2001] and [Groner, *et al.* 2002]. New spectra of acetone and acetic acid will then be recorded where necessary in order to analyze and interpolate the ground and low-energy states of these species as well.

Identification and assignment of excited state features in acquired spectra will be accomplished with several techniques including; (1) spectral parameter fitting, (2) variation of cell temperature to study intensity variations, and (3) comprehensive ground state assignments that remove ambiguity in excited state assignments.

The chemicals necessary for the proposed work are available in the laboratory in pure forms. Acetone and acetic acid are volatile liquids that can be placed in a glass sample container exterior to the spectrometer and flowed through the free space cell. Dimethyl ether is an explosive, highly volatile gas, that can be regulated with standard gas control valves and flowed through the apparatus analogously to the volatile liquids.

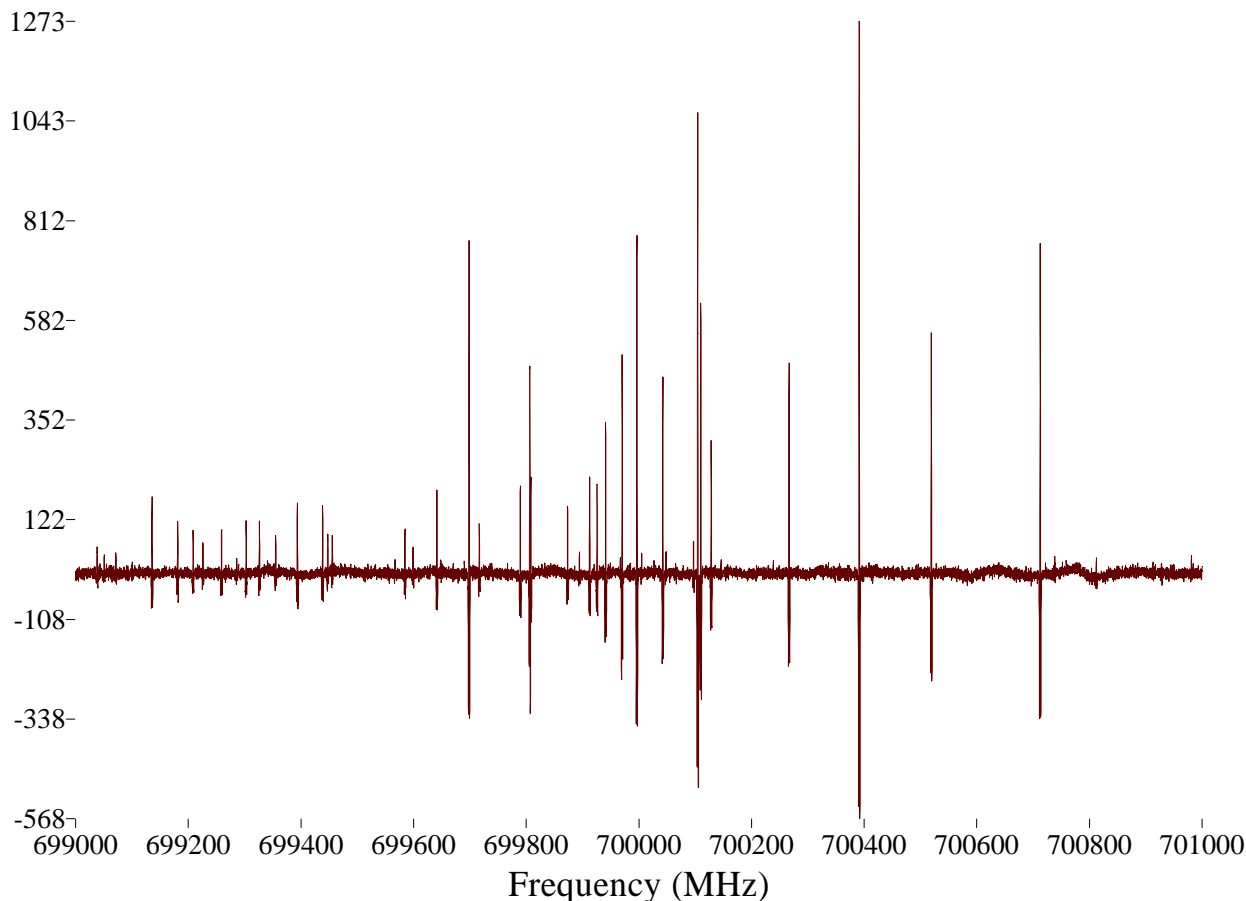


Figure 4: A 2 GHz survey scan of methyl cyanide (CH_3CN) at $429\ \mu\text{m}$.

Wide frequency survey scans of 2-50 GHz can be performed over 1/2 hour to 20 hour time periods. These scans will quickly identify the prominent (ground state) features of rotational spectra such as R and Q branches. Comprehensive sweeps will ensure that the analogous vibrational-torsional state R and Q branches will be identified. Reliable rest frequencies can be obtained directly from the survey scans. A survey scan that shows 2 GHz of the $429\ \mu\text{m}$ spectrum of methyl cyanide is shown in Figure 3. Physical limitations of frequency surveys are given by; (1) multiplier source tuning range, (2) cryogenic detector hold time (~ 40 hours, applies only above 170 GHz), (3) spectrometer $\text{N}_2(l)$ coolant supply (only for measurements $< 295\ \text{K}$).

Rest frequencies will be analyzed with the SPFIT/SPCAT program suite that is also available through this laboratory to the general public. The programs combine to provide both analysis of laboratory spectra, and comprehensive listings of accurate rest frequencies. Analysis often requires iterative fitting of data, followed by further rest frequency measurements, until the rest frequency listings are considered comprehensive. With the current state-of-the-art at this laboratory, comprehensive listings of ground and low energy excited states should become available up to 1 THz for each of the proposed species.

The analysis and rest frequencies will be published in peer reviewed literature. Furthermore, rest frequencies will be made available through the JPL Spectral Line Catalog online at <http://spec.jpl.nasa.gov/>.

3.3 Impact of the Proposed Work

The proposed work will directly impact our developing understanding of chemical evolution pathways in the universe beyond our solar system. Cosmochemistry to be done with the NASA telescopes **Herschel** and **SOFIA**, will rely on comprehensive rest frequency listings up to 1.8 THz for known astrophysical molecules. The current status of these listings for the proposed species is insufficient for detection/identification or avoidance of interference for a majority (50 - 80%) of the spectral features, due to these molecules, through 600 GHz. Above 600 GHz, this percentage soars rapidly to 100%. Comprehensive rest frequency listings, up to the state-of-the-art (currently about 1 THz), will be made available through the present proposed research. Furthermore, the vibrational-torsional state listings (and subsequent observations, of course) will also allow better thermodynamic and chemical kinetic understanding of the chemical systems these species are involved in.

The proposed studies provide **Herschel** and **SOFIA** with better means to study highly dense spatial and spectral regions of the interstellar medium. Successful observations that fully interpret the science will require the accurate rest frequencies that will be determined in the work proposed.

Observations based upon the results of the proposed work will directly address the Origins science objective of **Understanding how today’s Universe of galaxies, stars and planets came to be**; as well as the objective, **Learning how stars and planetary system form and evolve**. Observation of heavy organic molecules with key functional groups will be used to study the steps in the saturated carbon chemistry necessary for life as we know it. These observations will directly support the Origins science objective of **Understanding the diversity of other worlds and search for those that might harbor life**. The high quality rest frequencies generated under this proposal will allow spectral lines of these molecules to be used as highly sensitive tracers of the ISM conditions.

3.4 Relevance to NASA Programs

The NASA missions; **Herschel** and **SOFIA**, each have high resolution spectrometers (**Herschel** / **HIFI** has 134 - 1000 kHz resolution for 480 - 1900 GHz spectral regions) that will resolve individual molecular features throughout the submillimeter and into the Far-Infrared. These telescopes are the best source for spectral information above *ca.* 900 GHz where ground-based instruments are blinded by atmospheric absorption. The narrow beams available at shorter wavelengths (12 - 40”) are able to survey and examine dense interstellar regions with high spatial and spectral precision. Better pointing, frequency coverage and beam size culminate in astrophysical data that will be several orders of magnitude more sensitive than ground based observations [van Dishoeck, 2001].

These missions are developing along the cutting edge of submillimeter/Far-Infrared technology; therefore, few comprehensive rest frequency listings of organic compounds exist. Knowledge of molecular line parameters such as rest frequencies, intensities and state energies for KNOWN astrophysical molecules is required in order to accomplish the following NASA goals in **Astro-nomical Search for Origins**; *Trace the chemical pathways by which simple molecules and dust evolve into the organic molecules important for life*, and *Develop the tools and techniques to search for life on planets beyond our Solar System*. The molecules chosen for the proposed research are at the cutting edge of both cosmochemistry and spectroscopy. Simultaneous development of laboratory spectroscopy and observatories is required for achievement of these goals.

3.5 Summary

Three molecules; acetone, dimethyl ether, and acetic acid, have been proposed for intensive laboratory research and analysis to produce comprehensive rest frequency listings necessary for completion of NASA goals. These molecules are building blocks of organic chemistry and at the cutting edge of spectroscopic and cosmochemical knowledge. These molecules are known to exist in protostellar regions, where planetary systems and potential new life are evolving. The proposed species have particularly complex spectra, of which only the ground state rest frequencies below *ca.* 600 GHz are adequately characterized. Scientific questions to be addressed with high resolution spectrometers onboard NASA telescopes (*e.g.* SOFIA, HSO) regarding chemical compositions and elemental abundances will be hindered by unknown spectral features due to these KNOWN astrophysical molecules. The existing resources of the Jet Propulsion Laboratory - Molecular Spectroscopy group will be used to extend the state-of-the-art in both measurements and analysis. New laboratory spectra will be measured and analyzed with state-of-the-art submillimeter and Far-Infrared multiplier technology. The powerful SPFIT/SPCAT program suite will be used to model the quantum-mechanical interactions that generate the complexity of these molecular spectra. All of this will culminate in extension of the ground state listings, as well as new comprehensive analyses of low energy vibrational-torsional states.

Work will begin in calendar year 2004 and require significant analysis time for each species. Therefore the following schedule is expected:

2004

- Analysis of existing literature data
- Train postdoctoral fellow in spectrometer operation
 - Measurements of dimethyl ether at 600 - 900 GHz
 - Measurements of acetone at 600 - 900 GHz
 - Measurements of acetic acid at 400 - 900 GHz
- Train postdoctoral fellow with SPFIT/SPCAT analysis software
 - Analysis of (new) ground state spectra

2005

- Analysis of dimethyl ether excited vibrational torsional states
 - publish results of dimethyl ether study
- Implement new technology available through JPL collaborations
 - Extend measurements of each species
- Analysis of acetone excited vibrational torsional states
 - Publish results of acetone study

2006

- Implement new technology available through JPL collaborations
 - Extend measurements of each species
 - improved/extended rest frequencies will be made available through www/ftp server
- Analysis of acetic acid excited vibrational torsional states
 - Publish results of acetic acid study

4 Management Plan

The principal investigator, Brian J. Drouin Ph.D., will engage in the proposed research as a significant portion (25%) of his work plan. A postdoctoral two-year appointment will be advertised with an optional third year. Acceptable candidates will be required to have experience in high-resolution molecular spectroscopy and interpretation of rotationally resolved molecular spectra. The postdoctoral fellow will be trained by the principal investigator for both rest frequency measurements and analyses. The \$107 - \$117K/year budget is primarily devoted to employee time, this corresponds to 75% of one full time employee (1330 productive work hours).

The work will be done with the spectrometer and software at the Millimeter, Submillimeter and Far-Infrared Spectroscopy Laboratory at the Jet Propulsion Laboratory. The personnel necessary for the task completion are the principal investigator and a postdoctoral associate. During the first year of the proposed task the postdoctoral associate will be trained in both operation of the spectrometer and analysis software. This training will use dimethyl ether as both a case in need of further study and a starting point for the more involved analyses expected to be necessary for acetic acid and acetone spectra. Further work in the second and third year of the task will focus heavily on analysis of acetone and acetic acid spectra, as well as push the state-of-the-art (upper frequency limit) through collaborations within JPL.

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6 Facilities and Equipment

The laboratory facilities and equipment are sufficient for completion of the proposed task. Apparatus includes both capital equipment and rented equipment. No new apparatus beyond those used in conjunction with collaborative projects at JPL are expected to be needed to complete the projected work schedule. Rental charges will be shared with the UARP task.

Capital equipment used in this experiment:

Agilent sextupler (83558A): \$16K

Infrared Labs InSb detector and Dewar: \$10K

Rented equipment used in this experiment:

Sweep Synthesizer (HP 8314B): \$11K/year

Lock-In-Amplifier (SR 830): \$3K/year

In the event of a capital or rental equipment failure there are back up systems available in this laboratory (a second sweep synthesizer) and in other JPL laboratories (several other Agilent sextuplers). Some rental equipment can be replaced with similar equipment, but not necessarily similar rent, through the intra-laboratory instrument loan-pool.

7 Brian Drouin Curriculum Vitae

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Dr. B. J. Drouin completed a double major B.S. in Chemistry and Mathematics at the University of Wisconsin-Madison in 1995. He received his Ph.D. from the University of Arizona in 1999 from research director Stephen Kukolich for microwave spectroscopy of organometallic compounds. The thesis work involved measurement and analyses of highly precise rotational transition frequencies of molecules in cold molecular beams. In 1999 he became a California Institute of Technology Postdoctoral Scholar at the Jet Propulsion Laboratory. At JPL he has recorded and analyzed submillimeter spectra of both astrophysical and atmospheric molecules while incorporating state-of-the-art hardware and software to the submillimeter spectrometer. He is now a JPL scientist and is responsible for measurements of molecular line-shape parameters for the Microwave Limb Sounder.

Research Experience

California Institute of Technology, Jet Propulsion Laboratory, Pasadena, CA.

2000 - present, principal Investigator: Dr. E. A. Cohen - Measure pressure and temperature dependencies of rotational transition lineshapes in support of MLS.

1999 - present, principal Investigator: Dr. H. M. Pickett - Far-Infrared, submillimeter and microwave spectroscopy of atmospheric and astrophysical molecules.

Department of Chemistry, University of Arizona, AZ

1995 - 1999 Research Director: Dr. S. G. Kukolich - Dissertation Title: Microwave Spectra and Structures of Organometallic Compounds

Department of Chemistry, University of Wisconsin-Madison, WI

1994 - 1995 Research Director: Dr. D. F. Gaines - Syntheses and characterizations of boron hydrides and allyl silanes.

1995 - 1995 Research Director: Dr. J. C. Wright - Development of a computer interface for an optical parametric oscillator.

1992 - 1993 Research Director: Dr. J. C. Wright - Synthesis and mass-spectrometric characterization of $C_{60}H_{36}$ and $C_{70}H_{36}$.

Department of Horticulture, University of Wisconsin-Madison, WI

1994 - 1995 Research Director: Dr. B. McCown - Preparation of microculture gels and micro-propagation of genetically engineered yew, thuja and cranberry species.

8 Publication List for Brian Drouin

- 1) S.L. Widicus, B. J. Drouin, K.A. Dyl, G.A. Blake, Millimeter wavelength measurements of the rotational spectrum of 2-aminoethanol, *J. Molec. Spectrosc.*, 217(2), 278-281, 2003.
- 2) P. Groner, S. Albert, E. Herbst, F. C. DeLucia, F. J. Lovas, B. J. Drouin, J. C. Pearson, Acetone: Laboratory Assignments And Predictions Through 620 GHz For The Vibrational-Torsional Ground State, *Ap. J. Supp.*, 142, 145 2002.
- 3) M. M. Yamada, M. Kobayashi, H. Habara, T. Amano, B. J. Drouin, Submillimeter-wave Measurements of the Pressure Broadening of BrO., *J. Quant. Spectrosc. Radiat. Trans.*, *in press*, 2003.
- 4) B. J. Drouin, R. R. Gamache, J. Fischer, Temperature dependent pressure induced lineshape of O₃ rotational transitions in air, *J. Quant. Spectrosc. Radiat. Trans.*, *in press* 2003.
- 5) B. J. Drouin, Temperature Dependent Pressure Induced Lineshape of the HCl $J = 1 \leftarrow 0$ Rotational Transition in Nitrogen and Oxygen, *J. Quant. Spectrosc. Radiat. Trans.*, *in press* 2003.
- 6) G. C. Toon, J.-F. Blavier, B. Sen and B. J. Drouin, Atmospheric COCl₂ measured by solar occultation spectrometry, *Geophys. Res. Lett.*, 28, No. 14 , p. 2835. 2000.
- 7) B. J. Drouin, C. E. Miller and E. A. Cohen, Further investigations of the submillimeter spectrum of ClO, *J. Molec. Spectrosc.* 207(1), p. 4, 2001.
- 8) C. E. Miller and B. J. Drouin, The X₁²Π_{3/2} and X₂²Π_{1/2} Potential Energy Surfaces of FO, *J. Molec. Spectrosc.*, 205(2), p. 312, 2001.
- 9) B. J. Drouin, C. E. Miller, H. S. P. Müller and E. A. Cohen, The rotational spectra, isotopically independent parameters, and interatomic potentials for the X₁²Π_{3/2} and X₂²Π_{1/2} states of BrO, *J. Molec. Spectrosc.*, 205(1), p. 128, 2001.
- 10) S. G. Kukolich, B. J. Drouin, O. Indris and J. J. Dannemiller, J. P. Zoller and W. A. Herrmann, Microwave spectra, DFT calculations and molecular structure of acetylenemethyldioxorhenium, *J. Chem. Phys.*, 113, p. 7891, 2000.
- 11) B. J. Drouin, J. J. Dannemiller and S. G. Kukolich, Structural characterization of 'syn' and 'anti' - allyltricarbonylbromide, analyses of rotational spectra, quadrupole coupling and density functional calculations, *Inorg. Chem.*, 39(4), p. 827-835, 2000.
- 12) B. J. Drouin, J. J. Dannemiller and S. G. Kukolich, The gas-phase structure of chloroferrocene from microwave spectra, *J. Chem. Phys.*, 112(2), p. 747, 2000.
- 13) B. J. Drouin and S. G. Kukolich, Microwave spectra and the molecular structure of tetracarbonyl ethyleneiron, *J. Am. Chem. Soc.*, 121(16), p. 4023, 1999.
- 14) T. G. Lavaty, P. Wikrent, B. J. Drouin and S. G. Kukolich, Microwave measurements and calculations on the molecular structure of tetracarbonyldihydorruthenium, *J. Chem. Phys.*, 109 (21), p. 9473, 1998.
- 15) S. G. Kukolich, B. J. Drouin, P. A. Cassak and J. L. Hubbard, Microwave measurements and calculations on cyclopentadienyl rhodium dicarbonyl, a V₁₀ hindered rotor, *Organometallics*, 17 (18), p. 4105, 1998.
- 16) B. J. Drouin and S. G. Kukolich, The molecular structure of tetracarbonyldihydroiron, microwave measurements and density functional theory calculations, *J. Am. Chem. Soc.*, 120 (27), p. 6774, 1998.
- 17) B. J. Drouin, P. A. Cassak and S. G. Kukolich, Microwave measurements of rhenium quadrupole coupling in cyclopentadienyl rhenium tricarbonyl, *J. Chem. Phys.*, 108 (21), p. 8878, 1998.

- 18)** B. J. Drouin, J. F. Madden, R. S. Glass, M. Barfield and S. G. Kukolich, Determination of the gas phase conformation of 1,4,7-trithiacyclononane, *J. Phys. Chem.*, 101 (48), p. 9180, 1997.
- 19)** B. J. Drouin, P. A. Cassak, T. G. Lavaty and S. G. Kukolich, Measurement of structural and quadrupolar coupling parameters for bromoferrocene using microwave spectroscopy, *J. Chem. Phys.*, 107 (17), p. 6541, 1997.
- 20)** B. J. Drouin, P. A. Cassak, P. M. Briggs and S. G. Kukolich, Determination of structural parameters for the half-sandwich compounds cyclopentadienyl thallium and cyclopentadienyl indium and indium quadrupole coupling for cyclopentadienyl indium using microwave spectroscopy, *J. Chem. Phys.*, 107 (10), p. 3766, 1997.
- 21)** P. Wikrent, B. J. Drouin, S. G. Kukolich, J. C. Lilly, M. T. Ashby, W. A. Hermann and W. Scherer, Measurements of the structure of methyltrioxorhenium using microwave spectroscopy, *J. Chem. Phys.*, 107 (7), p. 2187, 1997.
- 22)** B. J. Drouin, P. A. Cassak and S. G. Kukolich, Measurement of structural and quadrupolar coupling parameters for chloroferrocene using microwave spectroscopy, *Inorg. Chem.*, 36, p. 2868, 1997.
- 23)** S. M. Sickafoose, P. Wikrent, B. J. Drouin, S. G. Kukolich, Microwave spectra and quadrupole coupling measurements for methyl rhenium trioxide, *Chem. Phys. Lett.*, 263, p. 191, 1996.

9 Current and Pending Research Support

Dr. Brian Drouin is currently supported through the Earth Observing System (EOS) Spectroscopy Program and the Microwave Limb Sounder (MLS) Mission. MLS support will continue through the next funding cycle. He expects to receive new support in the next funding cycle (FY '04 - FY '06) from Astronomy and Physics Research and Analysis (APRA) as well as through continued support (turned over from PI Edward Cohen) from the Upper Atmospheric Research Programs (UARP). A summary of current and Pending Awards, Commitments (%FTE), as well as Point of contacts (POCs) are listed in the table below.

Current	Role	%FTE	POC	Telephone	email
EOS	Co-Investigator	60%	David Starr	(301) 614-6191	David.Starr@nasa.gov
MLS	Co-Investigator	40%	Joe Waters	(818) 354-3025	Joe.W.Waters@jpl.nasa.gov
Pending					
APRA	Principal Investigator	25%	David Bohlin	(202) 358-1544	j.david.bohlin@nasa.gov
UARP	Principal Investigator	50%	Michael Kurylo	(202) 358-0237	michael.j.kurylo@nasa.gov
MLS	Co-Investigator	25%	Joe Waters	(818) 354-3025	Joe.W.Waters@jpl.nasa.gov

10 Budget Summary

The budget includes support for employee desktop networking (\$3.0K/yr), for documentation and publication (\$1.0K/yr) and for travel expenses (\$2.0K FY '04 and FY '05, \$5.0K FY '06). Equipment rental is estimated to cost \$5.0K/yr and cryogenic supplies \$3.0K/yr. The remainder of the proposed budget covers the employee (25% FTE) and postdoctoral salaries (50% FTE) as well as overhead. Participation in the International Symposium for Molecular Spectroscopy at The Ohio State University is allotted in the travel budget for all three years for both the principal investigator and postdoctoral fellow. More travel funds are requested for the final year to allow for further presentation of results to the astronomy community (IAU Symposia, AAS meetings). The table below itemizes the cost plan. A more detailed spreadsheet that shows JPL salaries and services with their respective overhead formulae is attached.

Expense	Specific	Cost (Thousands of Dollars)		
		FY 04	FY 05	FY 06
Salary	Brian Drouin	\$29.0	\$30.8	\$32.5
Salary	Postdoctoral Fellow	\$37.5	\$38.0	\$39.0
Service	Desktop Network Support	\$ 3.0	\$ 3.0	\$ 3.0
Service	Documentation and Publication	\$ 1.0	\$ 1.0	\$ 1.0
Service	Equipment Rental	\$ 5.0	\$ 5.0	\$ 5.0
Service	Cryogenic Supplies	\$ 3.0	\$ 3.0	\$ 3.0
Travel	Meeting Attendance	\$ 2.0	\$ 2.0	\$ 5.0
Overhead	Multi-Program Support	\$ 5.9	\$ 6.3	\$ 6.7
Overhead	Labor Burden	\$ 9.8	\$10.1	\$10.3
Overhead	Contracting	\$ 1.0	\$ 1.0	\$ 1.0
Overhead	Purchasing	\$ 0.9	\$ 0.9	\$ 0.9
Overhead	G & A Burden	\$ 7.3	\$ 7.6	\$ 8.5
Overhead	Award Fee	\$ 1.5	\$ 1.4	\$ 1.5
Total		\$106.9	\$110.1	\$117.4